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Photoassisted Deposition of Silicon Dioxide from Silane and Nitrogen Dioxide

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This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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Three new reactions for depositing silicon dioxide at low temperatures using vacuum ultraviolet and ultraviolet radiation to initiate a reaction between silane and nitrogen dioxide have been developed. The optical and electrical properties of these films are reported. The effect of ion implantation on the infrared spectra of oxides grown by vacuum ultraviolet irradiation is also presented.

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PREFACE

We wish to thank Dr. J. F. Knudsen for the ion implants and G. A. To for obtaining the infrared spectra.

CONTENTS

I. INTRODUCTION

Thin films of silicon dioxide are used extensively as insulators in the fabrication of many semiconductor devices. Silicon dioxide films deposited by chemical vapor deposition typically require temperatures near 800° C. However, some processes, such as the fabrication of devices with multilevel aluminum interconnects, require deposition temperatures below 350° C. Several techniques have been developed for low-temperature deposition of silicon dioxide, including plasma-assisted deposition (Ref. 1), remote plasma-assisted deposition (Ref. 2), low-pressure chemical vapor deposition (Ref. 3), and photoassisted chemical vapor deposition (Ref. 4,5). Films deposited with some of these reactions have been found to have adhesion problems and tend to be incompletely oxidized. Several other deposition reactions using photodissociation of molecular oxygen (Ref. 6) or disilane (Ref. 7) have been reported. In this paper, we report three new reactions in which vacuum ultraviolet (VUV) light (1066 Å) and ultraviolet light (3000 Å) are used to initiate a reaction between nitrogen dioxide and silane or disilane, thus forming silicon dioxide. The effect of boron implantation on films grown by these reactions is also reported.

II. EXPERIMENTAL TECHNIQUE

The reactions were all carried out in a low-pressure vacuum system. Vacuum ultraviolet photoassisted silicon dioxide films (VUVOX) were deposited by initiating a reaction between silane and nitrogen dioxide with 1066 Å radiation. A microwave-excited (2.4 GHz) windowless argon discharge lamp was used as a light source. The partial pressures of argon and NO_2 were 3.0 and 0.25 Torr, respectively. The flow rates of silane and nitrogen dioxide were 3 and 50 sccm, respectively. In all the depositions, the samples were placed on a heated stage (100° C) 6 cm from the end of the lamp. The growth rate was 50 to 100 Å per minute.

A reaction between nitrogen dioxide and silane can also be initiated by longer wavelength (ultraviolet) radiation (UVOX). Nitrogen dioxide was decomposed using 3000 to 4000 Å radiation from a 1000-W, high-pressure xenon arc lamp. The output of the arc lamp was passed through a bandpass filter and focused to a 1-in. diameter spot on the sample. The pressure of nitrogen dioxide was 0.9 Torr, and the flow rates of silane and nitrogen dioxide were 3 and 50 sccm, respectively. The growth rate of these films was 100 to 200 Å per minute at 100° C.

Disilane was reacted with nitrogen dioxide (DSOX) in the presence of 2537 Å radiation from a low-pressure mercury grid lamp. The total pressure in the cell was 0.5 Torr, and the stage temperature was 100° C. The flow rates of disilane and nitrogen dioxide were 6 and 50 sccm, respectively. Under these conditions, disilane and nitrogen dioxide react rapidly (growth rates of 50 to 100 Å per minute) even in the absence of light. With 2537 Å light present, the growth rate increases by a factor of four.

For comparison purposes, films were also grown using remote plasma chemical vapor deposition (RPCVD) (Ref. 2). In these experiments, N_2O was dissociated using a microwave discharge; the N_2O pressure was 300 mTorr. Silane was introduced into the chamber downstream of the discharge at a flow rate of 1 sccm.

The index of refraction of the silicon dioxide films was measured with a Gartner manual ellipsometer using the 632.8-nm line of a He-Ne laser. Infrared spectra were recorded in the reflection mode on a Nicolet MX-1 Fourier transform spectrometer. Interface state density was determined by modeling the high-frequency (1 MHz) capacitance vs voltage curves. The boron implantation was done using a model 400 MPR-Veeco/AI ion implanter. The dose of implanted ions was 2×10^{15} cm^{-2}, and the samples were maintained at ambient temperature during the implants.

III. FILM PROPERTIES

The index of refraction of the VUVOX films was between 1.46 and 1.47. The SiO stretch in the infrared spectrum was at 1080 cm^{-1}, consistent with previous measurements of fully oxidized SiO_2 (Ref. 2). The electrical characterization of these films is reported elsewhere (Nss < 10^{11}, Qss < 10^{11}) (Ref. 8). The index of refraction of films grown by reacting NO_2 and silane in the presence of 3000 to 4000 Å light was 1.45 to 1.47. The maximum of the SiO stretching peak was lower than that of the VUVOX film (1075 cm^{-1}), indicating that either the films were not fully oxidized, or that the density was different. The interface state density of these films was determined to be between 5×10^{10} and $5 \times 10^{11}/cm^2$. The total amount of fixed charge was less then $10^{11}/cm^2$. The samples grown from the reaction of disilane and nitrogen dioxide in the presence of 2537 Å radiation had a considerably lower SiO stretching frequency (1068) and a lower index of refraction (1.44). These films also showed a medium strength peak at 871 cm^{-1} that probably corresponds to a SiN stretch, and a peak at 2300 cm^{-1} that is SiH. The combination of both a lower index of refraction and a lower SiO stretching frequency indicates that these films are both less dense and nonstoichiometric (Ref. 9). The comparison sample grown by RPCVD had an index of refraction of 1.46 and a SiO stretching frequency of 1080 cm^{-1}.

Upon implantation of boron ions, the SiO stretch in the VUVOX sample was observed to decrease by 12 cm^{-1}, and the full width at half maximum (FWHM) increased by 20 cm^{-1}. There was no change in the index of refraction within our experimental uncertainty. In the sample grown from the reaction of disilane and nitrogen dioxide (DSOX), there was a large change in both the index of refraction and the SiO stretching frequency upon implantation. The RPCVD-grown sample showed a decrease in the SiO stretching frequency of 7 cm^{-1}, no noticeable change in the FWHM, and an increase in the index of refraction from 1.46 to 1.48. The results of the implantation studies are summarized in Table I.

Table I. Effect of Boron Implantation on Index of Refraction and Infrared Absorption Peaks in Deposited Silicon Dioxide

Sample	Implant Energy	d (μm)	n	SiO Stretch ν (cm^{-1})	FWHM (cm^{-1})
VUVOX-1	Before implant	0.189	1.46	1080	62
	100 keV	0.173	1.46	1068	83
VUVOX-2	Before implant	0.167	1.46	1077	62
	150 keV	0.166	1.46	1068	83
UVOX-1	Before implant	0.103	1.46	1075	60
	100 keV	0.108	1.48	1066	96
DSOX-1	Before implant	0.227	1.44	1068	110
	100 keV	0.186	1.52	1045	159
RPCVD-1	Before implant	0.175	1.46	1082	80
	100 keV	0.175	1.48	1075	80

IV. DISCUSSION

A. REACTION MECHANISMS

There are several reactions that occur in the growth of these silicon dioxide films. Silane is photodissociated at wavelengths below 1700 Å with a maximum in the cross section at 1150 Å (Ref. 10). This gives silane radicals which can then react with the NO_2, giving SiO_2 (reaction 1).

$$\begin{aligned} SiH_4 + h\nu &\longrightarrow SiH_3 + H \\ SiH_3 + SiH_3 &\longrightarrow SiH_2 + SiH_4 \\ SiH_2 + 3\ NO_2 &\longrightarrow SiO_2 + H_2O + 3\ NO \end{aligned} \qquad (1)$$

NO_2 will also photodissociate at these wavelengths, giving atomic (^1D) and molecular oxygen (Ref. 11). This oxygen can then react with the silane to form SiO_2 (reaction 2).

$$\begin{aligned} NO_2 + h\nu &\longrightarrow NO + O \\ NO_2 + O &\longrightarrow NO + O_2 \\ SiH_4 + 4\ O &\longrightarrow SiO_2 + 2\ H_2O \end{aligned} \qquad (2)$$

This second reaction sequence is probably not very important since use of 1849 Å radiation does not result in any silicon dioxide film growth at the same operating pressure, even though NO_2 has a significant photodissociation cross section at this wavelength. When the NO_2 partial pressure is increased, a fine white powder is observed to grow on the walls of the chamber and on the window. These results are consistent with the very rapid reaction ($k = 1 \times 10^{-10}$ cm^3 mol^{-1} sec^{-1}) (Ref. 12) of atomic oxygen (^1D) with NO_2 to form O_2 and NO. Thus, any atomic oxygen formed

from the dissociation of NO_2 reacts to form molecular oxygen. The reaction of molecular oxygen with silane is considerably slower than the reaction of silane radicals with NO_2. This then explains why there is little growth with irradiation at 1849 Å compared to the rapid growth observed with argon irradiation.

When 3000 to 4000 Å radiation is used, NO_2 photodissociates to form NO and O (^3P). The reaction rate of O (^3P) with NO_2 is about three orders of magnitude slower than the rate of reaction of O (^1D) ($k = 9 \times 10^{-12}$ cm^3 sec^{-1} mol^{-1}) (Ref. 12). The reaction rate of silane with O (^3P) is very rapid, thus accounting for the rapid growth during irradiation with 3000 to 4000 Å light.

B. IMPLANTATION EFFECTS

Upon ion implantation with boron, the wavelength of the SiO stretch in the VUVOX films was observed to decrease by about 10 cm^{-1}. A portion of the infrared spectra of a VUVOX film before and after implantation with 100 keV boron ions is shown in Fig. 1. This decrease can be caused by both densification and a change in the stoichiometry of the film. The FWHM of the SiO stretch for these films increased by 20 cm^{-1} upon implantation. It has been previously reported (Ref. 2) that suboxide films with more Si-Si bonds have broader linewidths. However, the linewidth of the fully oxidized films in these previous studies corresponds to the linewidth of our films after implantation. We cannot, therefore, use these observations to determine which mechanism is causing the change in the infrared spectra of our films. It has been reported (Ref. 13) that both densification and dislocation damage occur during ion implantation, and it is likely that both effects are occurring in our films. The RPCVD films had about the same initial SiO stretching frequency, and the change in frequency upon implantation was smaller than that in the VUVOX films (7 cm^{-1}). The FWHM of the RPCVD-grown films did not change any upon implantation; however, the linewidth was initially 20 cm^{-1} greater than that of the VUVOX films. Thus, any change caused by the implant may be smaller than the intrinsic linewidth of the films grown by this method. It is observed that films

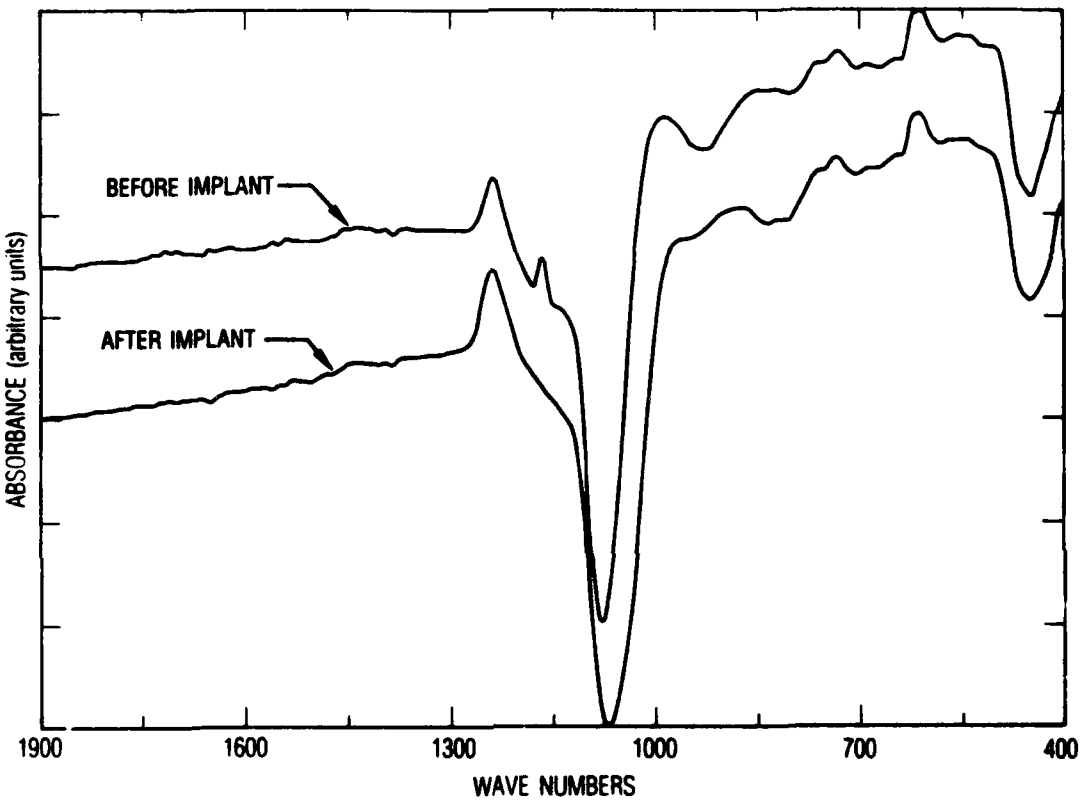

Fig. 1. Infrared Spectra of VUVOX Films Before and After Implantation with 100 keV Boron Ions

with lower SiO stretching frequencies (i.e., DSOX) show the greatest change upon implantation. This is consistent with nonstoichiometric films being more subject to damage by the implant. We have not yet been able to determine why the RPCVD and VUVOX films are affected differently by ion implantation.

V. SUMMARY

We have demonstrated two new reactions for depositing silicon dioxide using vacuum ultraviolet and ultraviolet radiation to induce a reaction between silane and nitrogen dioxide. These reactions produce high-quality, fully oxidized silicon dioxide with good electrical and mechanical properties. The optical properties of the vacuum ultraviolet-deposited films are found to change slightly after ion implantation. Other films with lower SiO stretching frequencies show large changes upon implantation.

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LABORATORY OPERATIONS

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